

(19)



Europäisches Patentamt

European Patent Office

Office européen des brevets



(11)

EP 0 489 561 B1

(12)

EUROPEAN PATENT SPECIFICATION

(45) Date of publication and mention
of the grant of the patent:
06.03.1996 Bulletin 1996/10

(51) Int. Cl.⁶: **B44F 1/04**, G09F 13/20

(21) Application number: **91311189.4**

(22) Date of filing: **02.12.1991**

(54) Articles exhibiting durable fluorescence

Gegenstände, die dauerhafte Fluoreszenz zeigen

Articles montrant une fluorescence durable

(84) Designated Contracting States:
AT CH DE ES FR GB IT LI NL

(30) Priority: **06.12.1990 US 624195**

(43) Date of publication of application:
10.06.1992 Bulletin 1992/24

(73) Proprietor: **MINNESOTA MINING AND
MANUFACTURING COMPANY**
St. Paul, Minnesota 55133-3427 (US)

(72) Inventors:
• **Pavelka, Lee A.,**
c/o Minnesota Mining and
St. Paul, Minnesota 55133-3427 (US)
• **Burns, David R.,**
c/o Minnesota Mining and
St. Paul, Minnesota 55133-3427 (US)

- **Johnston, Raymond P.**
Minnesota Mining &
St. Paul, Minnesota 55133-3427 (US)
- **Shinbach, Edward S.**
Minnesota Mining &
St. Paul, Minnesota 55133-3427 (US)

(74) Representative: **Baillie, Iain Cameron et al**
c/o Ladas & Parry
Altheimer Eck 2
D-80331 München (DE)

(56) References cited:
WO-A-89/02637 **US-A- 3 830 682**
US-A- 4 424 449 **US-A- 4 443 226**

- **PATENT ABSTRACTS OF JAPAN 26 March 1990**
&JP-A-2 016 042 (NIPPON CARBIDE IND CO INC
) 19 January 1990

EP 0 489 561 B1

Note: Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European Patent Convention).

Description

Field of Invention

5 The present invention relates to articles which exhibit durable fluorescence, and in one embodiment relates particularly to retroreflective sheetings which exhibit durable fluorescence.

Background

10 Retroreflective signs have achieved widespread use for safety and informational signs along roads because of the high nighttime visibility they provide. In order to enhance the daytime visibility of such signs, it has been suggested to make the signs fluorescent as well as retroreflective. U.S. Patent No. 3,830,682 (Rowland) discloses cube-corner type retroreflective sheetings which incorporate fluorescent dyes, e.g., rhodamine and fluorescein dyes. The resultant signs provide fluorescent ambient appearance and bright, colored retroreflection.

15 A problem with fluorescent retroreflective sheetings is that upon, in some cases relatively moderate, exposure to solar radiation, such as is encountered in sunlit outdoor applications, the fluorescent properties of the sheetings degrade. Many fluorescent dyes tend to fade or become colorless. This loss in fluorescent performance causes the ambient color of the subject sheeting to fade as well as changing the retroreflective appearance of the sign, thereby impairing the effectiveness of the sign and reducing the potential safety benefits thereof. In some instances, such degradation can
20 occur over as short a time as six months.

U.S. Patent No. 3,830,682 (Rowland) discloses retroreflective articles comprising synthetic plastic resins and fluorescent dyes such as rhodamine and fluorescein dyes.

Japan Kokai No. 2-16042, Application No. 63-165914 (Koshiji et al.) discloses fluorescent articles comprising a screen layer and a layer containing a fluorescent coloring agent wherein the screen layer permits a defined range of
25 transmission of light. According to the reference, the screen layer must have a transmittance of more than 30 percent at 370 nanometers and less than 20 percent at 340 nanometers. The reference further teaches that the coloring agent may be any fluorescent coloring agent and that the binder or matrix of the colored layer is subject to no critical limitation.

Summary of Invention

30 The present invention provides articles that exhibit a surprising enhancement in fluorescent durability, i.e., the fluorescent properties of the articles are retained longer than is expected, even upon prolonged exposure to direct sunlight. Sunlight, i.e., ground level solar radiation, comprises electromagnetic radiation having wavelengths within the range of about 290 nanometers up through visible light range.

35 In brief summary, fluorescent articles of the invention comprise a color layer having first and second sides and a screen layer disposed to the first side of said color layer, wherein:

- a) the color layer comprises a defined fluorescent dye dissolved in a defined polymeric matrix; and
- b) the screen layer being substantially transparent to visible light and comprising means for screening substantial
40 portions of ultraviolet radiation which is incident thereto.

The color layer and screen layer may be separate layers arranged in the defined manner or may be laminated together, either directly or with an intermediate adhesive layer.

45 In one particularly useful class of embodiments, the article is retroreflective and the color layer is substantially transparent, with the color layer either having retroreflective elements formed on its second, i.e., back side, or having a retroreflective base layer comprising retroreflective elements disposed on its second side.

Brief Description of Drawing

50 The invention will be further explained with reference to the drawing, wherein:

Figure 1 is a cross-sectional illustration of a portion of one retroreflective embodiment of the invention;
Figure 2 is a cross-sectional illustration of a portion of another retroreflective embodiment of the invention; and
Figure 3 is a cross-sectional illustration of another retroreflective embodiment of the invention.

55 These figures, which are idealized, are not to scale and are intended to be merely illustrative and non-limiting.

Detailed Description of Illustrative Embodiments

Figure 1 shows typical fluorescent article 10 of the invention comprising color layer 12 with first, i.e., front, side 14 and second, i.e., back, side 16 and overlay or screen layer 18 disposed on first side 14. In the embodiment illustrated, screen layer 18 is laminated directly to color layer 12. Article 10 is retroreflective, and color layer 12 has retroreflective elements 20, e.g., cube-corner retroreflective elements, formed therein.

Figure 2 shows another typical fluorescent article 30 comprising color layer 32 with first side 34 and second side 36 and screen layer 38 disposed on first side 34. In the embodiment illustrated, screen layer 38 is bonded to color layer 32 with intermediate adhesive layer 33. In order to render article 30 retroreflective, retroreflective base sheet 42 has been bonded to second side 36 with intermediate adhesive layer 40.

Color layers of articles of the invention comprise a defined daylight fluorescent dye dissolved in a defined polymeric matrix.

The polymeric matrix is typically preferably substantially transparent to visible light, particularly to light of the wavelengths emitted by the dye and light of the wavelengths which cause the dye to fluoresce. The polymeric matrix is selected from one or more of the following: polycarbonate, polyacrylic imide, polyester, or polystyrene. In embodiments wherein the color layer has reflective elements formed therein, e.g., cube-corner reflectors, polycarbonate is typically preferred because it tends to exhibit greater dimensional stability than polyester. Preferably, the matrix consists essentially of one of the indicated polymers. Color layers made with a single polymer matrix material will typically tend to exhibit greater transparency than will those made with substantial portions, e.g., 5 weight percent or more each, of two or more polymers. However, blends of two or more substantially transparent polymers that are substantially miscible are typically transparent and may be used herein.

The fluorescent dye, which is a daylight fluorescent dye, i.e., one which emits visible light upon exposure to light of a visible wavelength is selected from the following: thioxanthene dye, thioindigoid dye, benzoxazole coumarin dye, or perylene imide dye. If desired, a combination of such dyes may be used.

Typically, the color layer contains between about 0.01 and about 1.0, preferably between about 0.05 and about 0.3, weight percent of dye. Color layers that contain lower amounts of dye may not exhibit the degree of bright fluorescence which is desired. As will be understood by those skilled in the art, however, thicker color layers containing a specified loading of dye will typically exhibit brighter fluorescence and deeper color than do thinner color layers containing the same dye loading. Color layers which contain high levels of fluorescent dye may exhibit self-quenching phenomena. It has been observed that between two embodiments of the invention wherein the color layers have substantially equivalent initial fluorescent brightness and appearance, the first color layer being made with relatively greater thickness and a relatively lower dye loading and the second color layer being made with relatively thinner thickness and relatively higher dye loading, the color layer having the lower dye loading exhibited greater fluorescent durability than the other color layer. Both embodiments, however, exhibited greater fluorescent durability than expected.

In some instances, the dye in the color layer will consist essentially of thioxanthene, thioindigoid, benzoxazole coumarin, and/or perylene imide dyes. In other instances, however, the color layer may also contain coloring agents such as pigments or other dyes in addition to those described above to adjust the color and appearance of the article. For instance, polycarbonate typically has a slight yellowish cast or appearance and minor amounts, e.g., about 0.01 weight percent or less, of colorants sometimes referred to as "bluing agents" may be incorporated therein to yield a substantially colorless or "water white" appearance. Typically, the color layer will contain at most limited quantities of dyes other than those described above as other dyes typically do not exhibit desired durable fluorescence and color layers which contain high proportions thereof will be subject to detrimental effects upon prolonged exposure to sunlight. If desired, non-fluorescent dyes or pigments may also be used, however, such dyes should be selected so as to not undesirably interfere with the fluorescent performance of the daylight fluorescent dyes discussed above or with the overall appearance of the article. In the case of retroreflective articles, any non-fluorescent dyes or pigments used should not undesirably impair the transparency of the color layer.

In some embodiments, e.g., wherein the article is a retroreflective sheeting, the color layer is typically between about 2 and about 25 mils (50 and 625 micrometers) thick as such thicknesses offer a useful balance of cost and performance, particularly for retroreflective embodiments. If desired, however, color layers having thicknesses outside this range may be made in accordance with the invention.

The screen layer is disposed to the first or front side of the color layer so as to shield same from ultraviolet radiation which is incident to the article. This is the side of the article which is displayed and is desirably fluorescent. In the case of retroreflective embodiments, this side exhibits retroreflective properties, i.e., light such as from vehicle headlights that is incident thereto is retroreflected. As shown in Figure 1, screen layer 18 may be in direct contact with color layer 12, or, as shown in Figure 2, screen layer 38 may be bonded to color layer 32 with intermediate layer 33, or, as shown in Figure 3, screen layer 58 may be arranged in front of color layer 52 substantially without contacting it. Preferably, the screen layer and color layer are substantially coextensive such that the screen layer protects substantially all of the color layer.

The screen layer and, if used, the adhesive intermediate to the screen layer and color layer, are preferably substantially transparent to visible light of the wavelength emitted by the fluorescent dye in the color layer as well as being substantially transparent to light of the wavelength which excites the dye. At ground level solar radiation comprises electromagnetic radiation having wavelengths greater than about 290 nanometers, with the range of about 400 to about 700 nanometers typically being considered the visible light range. Radiation having lower wavelengths is believed to be the most damaging to fluorescent durability of dyes in the color layer, thus the screen layer preferably blocks a substantial portion, i.e., at least about 10 percent, more preferably at least about 50 percent, and most preferably substantially all, of the incident radiation having a wavelength below about 340 nanometers, more preferably below about 370 nanometers, and most preferably below about 400 nanometers. Radiation of these ranges is a major cause of the loss of fluorescent brightness of fluorescent dyes in polymeric matrices. In some embodiments, the screen layer may even screen electromagnetic radiation having wavelengths above about 400 up to, but below, the wavelengths which excite the dye. Although such screen layers would provide more effective protection to the color layer, they would tend to have a colored appearance which must be taken into account when formulating the color of the color layer such that the resultant article is of desired color. If desired, tinting screen layers, color layers, and/or intermediate adhesive layers (if any) to screen selected visible wavelengths could be used to tune the fluorescent response of the article.

The screen layer comprises means for screening ultraviolet radiation; it may be made of a material that inherently screens radiation as desired, or it may comprise a matrix which contains a selected screening agent to impart desired characteristics thereto. If an intermediate adhesive is used, it may contain ultraviolet screening agent so as to function as a screen layer.

It has been observed that incorporating ultraviolet radiation screening agents in the color layer may tend to provide minor improvements in fluorescent durability of the fluorescent dye contained therein, but the effect is relatively minor in relation to the advantages provided by use of separate screen and color layers as provided herein.

Although we do not wish to be bound by this theory, it is believed that, by screening radiation as discussed above, the screen layer prevents an as yet undefined degradation and/or reaction between the dyes and polymeric matrix materials which would otherwise occur. Insofar as we know, the advantages of the present invention are attained through the use of the combinations of fluorescent dyes and polymeric matrix materials discussed herein.

As discussed above, in some embodiments, articles of the invention are retroreflective. Such capability may be achieved as shown in Figure 1 by forming retroreflective elements 20 on second side 16 of color layer 12, or alternatively as shown in Figure 2 by attaching retroreflective base sheet 42 to second 36 of color layer 32, either with transparent intermediate adhesive layer 40 as shown or by laminating the base sheet and color layer in direct contact with one another (not shown). As shown in Figure 2, retroreflective base sheet 42 comprises a member with cube-corner retroreflective elements formed on back side 46 thereof. In other embodiments, the retroreflective base sheet may comprise a microsphere-based retroreflective structure, e.g., comprising a monolayer of transparent microspheres and reflective means disposed on the opposite side of the monolayer as the color layer. For instance, a screen layer/color layer combination of the invention may be laminated to the front surface of the cover film of an encapsulated-lens retroreflective sheeting such as is disclosed in U.S. Patent No. 3,190,178 (McKenzie) or it may even be used as the cover film of an encapsulated-lens sheeting. In retroreflective embodiments, the color layer or at least that portion of it which is disposed in front of the retroreflective elements, i.e., between the retroreflective elements and the screen layer, should be substantially transparent to visible light.

Figure 3 illustrates another retroreflective embodiment of the invention wherein the article of the invention is a "button-type" retroreflector. Article 50 comprises color layer 52 with first side 54 and second side 56, screen layer 58 disposed to first side 54, and base member 60, with screen layer 58 and base member 60 enclosing color layer 52. Second side 56 has retroreflective elements 62 formed therein. Screen layer 58 and color layer 52 can be disposed spaced apart from one another as shown, or alternatively may be placed in contact with one another. Article 50 can be mounted on a backing (not shown), e.g., a sign panel, such that first side 54 is presented for viewing and retroreflective effect, with screen layer 58 protecting the fluorescent durability of color layer 52 as described herein.

If desired, articles of the invention may be made in substantially rigid or flexible form. For example, in some embodiments the article may be sufficiently flexible to be wound about a mandrel having a diameter of about 1 centimeter.

Examples

The invention will be further explained by the following illustrative examples which are intended to be nonlimiting. Unless otherwise indicated, all amounts are expressed in parts by weight.

The following abbreviations are used in the examples:

Abbreviation	Meaning
AU	Acrylic urethane;
PAI	Polyacrylic imide;
PC	Polycarbonate;
PO	Polyolefin copolymer;
PEC	Polyester carbonate;
PET	Polyethylene terephthalate;
PMMA	Polymethylmethacrylate;
PS	Polystyrene;
PVC	Polyvinyl chloride (plasticized);
SCA	Solution cast acrylic;
RED GG	HOSTASOL RED GG - Solvent Orange 63 thioxanthene dye from Hoechst Celanese;
RED 5B	HOSTASOL RED 5B - Vat Red 41 thioindigoid dye from Hoechst Celanese;
LUMOGEN	LUMOGEN F240 Orange - perylene imide dye from BASF;
MACROLEX	MACROLEX 10GN - Solvent Yellow 160:1 benzoxazole coumarin dye from Mobay Corp.;
3G	HOSTASOL YELLOW 3G - Solvent Yellow 98 thioxanthene dye from Hoechst Celanese; and
GREEN GOLD	FLUOROL GREEN GOLD 084 - Solvent Green 5 perylene dye from BASF.

To simulate outdoor exposure to sunlight on an accelerated basis, in Examples 1-4 samples were exposed in accordance to ASTM G 26 - Type B, Method A, with a water-cooled xenon arc device with borosilicate inner and outer filters for periods of 102 minutes of exposure at a Black Panel temperature of about 63°C following by 18 minutes of exposure while subjecting the sample to deionized water spray. One thousand hours exposure on this device is believed to be equivalent to several months exposure to direct sunlight in an outdoor setting.

Unless otherwise indicated, the following test methods were used.

Color

Color was determined by one of two techniques as indicated.

In the first technique, referred to herein as "ISC", a Spectrosensor Integrating Sphere Colorimeter from Applied Color Systems was used at the following settings and conditions:

- D65 Illuminate,
- d/0 Geometry,
- Large Area View - Specular Included,
- 2 Degree Observer,
- 200 Percent Reflectance Setting,

with measurements being taken every 10 nanometers over a range of 400 to 700 nanometers.

In the second technique, referred to herein as "CSC", a Compuscan Colorimeter from Applied Color Systems was used at the following settings and conditions:

- D65 Illuminate,
- 0/45 Geometry,
- 30 millimeter port size,
- 2 Degree Observer,

with measurements being taken every 20 nanometers over a range of 400 to 700 nanometers.

ISC and CSC are believed to provide equivalent color definition results.

Peak Retention, was calculated as the ratio in percent of percentage reflectance of the sample after exposure for the indicated time to the percentage reflectance of the sample before exposure at the wavelength of the initial peak percentage reflectance.

The CIELAB color difference, Delta E, between the sample after exposure for the indicated period of time and the unexposed sample was determined. Delta E is a function of several color vector components. Accordingly, it should be understood that the Delta E results provided herein should be compared only within pairs of Samples wherein the color layers are equivalent as presented in the tables, but not between Samples of separate pairs. For instance, the Delta E obtained by Sample 5-1 can be meaningfully compared with Sample 5-A, but does not provide any meaningful significance with respect to the Delta E obtained with Sample 5-B or 5-2.

Retained Fluorescence

Fluorescence was determined using a SPEX Brand Fluorolog Spectrophotometer consisting of a xenon lamp powered by a ELXE 500 watt power supply, Model 1680 0.22 meter double spectrometer detector, Model 1681 0.22 meter spectrometer source, and a Products-for-Research Photomultiplier Model R298/115/381 operated by SPEX DM 300 software at a resolution of 2 nanometers.

Retained Fluorescence was calculated as the ratio in percent of fluorescent intensity of the sample after exposure for the indicated time to the fluorescent intensity of the unexposed sample, at the wavelength of peak emission of the unexposed sample.

Example 1

Example 1 illustrates the relationship between composition of polymer matrix of the color layer and utility of screen layer in accordance with the invention. In each of the samples, the color layer contained 0.2 weight percent of HOSTASOL Red GG, a thioxanthene dye.

In Sample 1-1 and Comparative Sample 1-A, the color layers consisted essentially of 12 mil (300 micrometer) thick extruded films of water white ultraviolet-stabilized polycarbonate, LEXAN 123R-112 from General Electric Company, believed to contain a small amount of blueing agent and mold release agent. In Sample 1-1, the screen layer was a 3 mil (75 micrometer) thick film consisting essentially of polymethyl methacrylate, LUCITE 47K from Du Pont, and 1.2 weight percent TINUVIN 327, a benzotriazole ultraviolet absorber from Ciba-Geigy. In Comparative Sample 1-A, a similar film without the ultraviolet absorber was used as the screen layer.

In Sample 1-2 and Comparative Sample 1-B, the color layers consisted essentially of 6 mil (150 micrometer) thick extruded films of KAMAX T-260, a polyacrylic imide from Rohm and Haas, to which 0.2 weight percent CYASORB UV 5411, a benzotriazole ultraviolet absorber from American Cyanamid, was added. In Sample 1-2, the screen layer was a 2 mil (50 micrometer) thick solvent cast film consisting essentially of an aliphatic acrylic polyurethane and 3 weight percent solids UVINUL 400, a benzophenone ultraviolet absorber from BASF, with a 1 mil (25 micrometer) thick layer of pressure-sensitive adhesive, isooctylacrylate/acrylic acid crosslinked with aziridine, on one side thereof. U.S. Patent No. 4,808,471 (Grunzinger) discloses such films and U.S. Patent No. Re. 24,906 (Ulrich) discloses such adhesives. In Comparative Sample 1-B, a similar film without the ultraviolet absorber was used as the screen layer.

In Sample 1-3 and Comparative Sample 1-C, the color layers consisted essentially of 6 mil (150 micrometer) thick extruded films of polyethylene terephthalate (intrinsic viscosity of 0.59 and molecular weight of about 20,000 to 25,000). In Sample 1-3 and Comparative Sample 1-C, the screen layers were like those used in Sample 1-2 and Comparative Sample 1-B, respectively.

In Sample 1-4 and Comparative Sample 1-D, the color layers consisted essentially of 6 mil (150 micrometer) thick extruded films of impact modified polystyrene, STYRON 615APR from Dow Chemical Company, to which 0.2 weight percent CYASORB UV 5411 was added. In Sample 1-4 and Comparative Sample 1-D, the screen layers were like those used in Sample 1-2 and Comparative Sample 1-B, respectively. The respective screen layers were bonded to the first sides of the color layers with an intermediate adhesive as in Sample 1-2 and Comparative Sample 1-B.

In Comparative Samples 1-E and 1-F, the color layers consisted essentially of 12 mil (300 micrometer) thick extruded films of LUCITE 47K, polymethyl methacrylate from Du Pont containing 0.2 weight percent CYASORB UV 5411. In Comparative Sample 1-E, the screen layer was like that used in Comparative Sample 1-B. In Comparative Sample 1-F, no screen layer was used.

In Comparative Samples 1-G and 1-H, the color layers consisted essentially of 6 mil (150 micrometer) thick extruded films of APEC DP9-9308NT, polyester carbonate from Mobay Corp. containing 0.2 weight percent of CYASORB UV 5411. In Sample 1-G, the screen layer was like that used in Sample 1-2. In Comparative Sample 1-H, a similar film without the ultraviolet absorber was used as the screen layer.

In Comparative Samples 1-I and 1-J, the color layers consisted essentially of 2 mil (50 micrometer) thick solution cast films of acrylic urethane. In Sample 1-I, the screen layer was like that used in Sample 1-2. In Comparative Sample 1-J, a similar film without the ultraviolet absorber was used as the screen layer.

In Comparative Samples 1-K and 1-L, the color layers consisted essentially of 3 mil (75 micrometer) thick solution cast films of plasticized polyvinyl chloride. In Sample 1-K, the screen layer was like that used in Sample 1-2. In Comparative Sample 1-L, a similar film without the ultraviolet absorber was used as the screen layer.

EP 0 489 561 B1

In Sample 1-1 and Comparative Samples 1-A, 1-E, and 1-F, the respective screen layer and color layer combinations were placed, with the screen layer in contact with the first side of the color layer, in a stamper shaped to form cube-corner retroreflective elements and stamped at about 204°C to form cube-corner retroreflective elements on the second surface of the color layer.

5 In Samples 1-2, 1-3, and 1-4 and Comparative Samples 1-B, 1-C, 1-D, 1-G, 1-H, 1-I, 1-J, 1-K, and 1-L, the screen layers were bonded to the first sides of the color layers with intermediate adhesive as described above. A retroreflective base sheet, SCOTCHLITE Brand Retroreflective Sheeting Diamond Grade No. 3970 from 3M, was then bonded to the second sides of the color layers with the same adhesive.

The results are tabulated in Table I.

10

Table I

Sample	Matrix ¹	Screen ²	Time ³	Peak Reten ⁴	Delta E ⁵	Retain Fluor ⁶
1-1	PC	Yes	1000	71	18	85
15 1-A	PC	No	1000	55	30	67
1-2	PAI	Yes	1000	84	14	90
1-B	PAI	No	1000	73	31	72
20 1-3	PET	Yes	1000	93	6	103
1-C	PET	No	1000	84	9	79
1-4	PS	Yes	500	77	21	NM ⁷
1-D	PS	No	500	68	29	NM ⁷
25 1-E	PMMA	Yes	1000	57	27	52
1-F	PMMA	None	1000	57	27	60
1-G	PEC	Yes	1000	69	20	76
30 1-H	PEC	No	1000	69	20	70
1-I	AU	Yes	500	48	84	NM ⁸
1-J	AU	No	500	47	88	NM ⁸
1-K	PVC	Yes	500	41	100	NM ⁸
35 1-L	PVC	No	500	40	100	NM ⁸

¹ Matrix polymer

² Whether screen layer contained UV screening agent, in 1-F no screen layer was used

³ Exposure time in hours

⁴ Peak Retention

40

⁵ CIELAB color difference determined by CSC

⁶ Retained Fluorescence

⁷ Not Measured, but Sample 1-4 was determined by visual inspection to have higher Retained Fluorescence than Sample 1-D

⁸ Not Measured, visually observed to have essentially no retained color

45

These results illustrate that the effectiveness of the invention is dependent upon the polymeric matrix material of the color layer.

50 Example 2

Example 2 illustrates changing the polymeric matrix of the screen layer.

In Samples 2-1, 2-2, and 2-3 and Comparative Samples 2-A, 2-B, and 2-C, the color layers consisted essentially of 12 mil (300 micrometer) thick extruded films of polycarbonate, LEXAN 123R-112 containing 0.12 weight percent of HOSTASOL RED GG. In Sample 2-4 and Comparative Sample 2-D, the color layers were similar except they contained 0.2 weight percent of the fluorescent dye.

55

In Sample 2-1 and Comparative Sample 2-A, retroreflective elements were embossed in the second sides of the color layers and then screen layers were bonded to the first sides of the color layers with an intermediate layer of adhesive

EP 0 489 561 B1

as used in some samples of Example 1. The screen layers were 2 mil (50 micrometer) thick films of acrylic polyurethane. In Sample 2-1 the screen layer contained 3 weight percent UVINUL 400.

In Sample 2-2 and Comparative Sample 2-B, retroreflective elements were embossed in the second sides of the color layers and then the screen layers were hot laminated directly to the first sides of the color layers. The screen layers were 2 mil (50 micrometer) thick films of ethylene/acrylic acid copolymer. In Sample 2-2 the screen layer contained an ultraviolet absorber.

In Sample 2-3 and Comparative Sample 2-C, retroreflective elements were embossed in the second sides of the color layers and then screen layers were solvent cast on the first sides of the color layers and dried. The screen layers were 0.8 to 1.0 mil (20 to 25 micrometer) thick films of solution cast acrylic, ACRYLOID B66 from Rohm and Haas. In Sample 2-3 the screen layer contained 1.2 weight percent TINUVIN 327.

In Sample 2-4 and Comparative Sample 2-D, retroreflective elements were embossed in the second sides of the color layers and polymethyl methacrylate screen layers were laminated to the first sides of the color layers as in Samples 1-1 and 1-A, respectively. The screen layers were 3 mil (75 micrometer) thick films of LUCITE 47K. In Sample 2-4 the screen layer contained 1.2 weight percent TINUVIN 327.

The percentage transmittance of the screen layers at the indicated wavelengths (in nanometers) was as follows:

Table IIa

Screen	Wavelength			
	400	370	340	300
2-1	84	43	0	0
2-A	78	75	69	59
2-2	80	2	0	0
2-B	84	77	70	67
2-3	87	10	1	1
2-4	89	88	88	86
2-4	56	0	0	0
2-D	87	81	71	67

The fluorescent durability results obtained with the resultant fluorescent articles are tabulated in Table IIb.

Table IIb

Sample	Matrix ¹	Screen ²	Time ³	Peak Reten ⁴	Delta E ⁵	Retain Fluor ⁶
2-1	AU	Yes	1000	85	7	91
2-A	AU	No	1000	76	12	85
2-2	PO	Yes	1000	89	7	103
2-B	PO	No	1000	79	13	86
2-3	SCA	Yes	1000	82	8	NM ⁷
2-C	SCA	No	1000	75	13	NM ⁷
2-4	PMMA	Yes	1000	77	15	85
2-D	PMMA	No	1000	64	23	67

¹ Matrix polymer of screen layer

² Whether screen layer contained UV screening agent

³ Exposure time in hours

⁴ Peak Retention

⁵ CIELAB color difference determined by CSC

⁶ Retained Fluorescence

⁷ Not Measured, but Sample 2-3 was determined to have higher Retained Fluorescence by visual inspection

EP 0 489 561 B1

These results illustrate that the effectiveness of the screen layer is dependent upon its screening properties and not its composition.

Example 3

5

Example 3 illustrates color layers containing different amounts of Red GG fluorescent dye in two different polymeric matrix materials.

In each sample, the color layer consisted essentially of a 12 mil (300 micrometer) thick extruded film of the indicated matrix polymer containing the indicated amount of dye. The samples were all exposed for 1000 hours.

10

The results are tabulated in Table III.

Table III

15

Sample	Matrix ¹	Dye ²	Screen ³	Peak Reten ⁴	Delta E ⁵	
3-1	PC	0.01	Yes	91	8	
3-A	PC	0.01	No	82	15	
3-2	PC	0.1	Yes	88	8	
3-B	PC	0.1	No	72	17	
20	3-3	PC	0.3	Yes	63	23
3-C	PC	0.3	No	41	43	
3-D	PMMA	0.01	Yes	63	44	
25	3-E	PMMA	0.01	No	71	31
3-F	PMMA	0.1	Yes	74	31	
3-G	PMMA	0.1	No	76	30	
30	3-H	PMMA	0.3	Yes	52	27
3-I	PMMA	0.3	No	51	27	

30

¹ Matrix polymer

² Weight percent of fluorescent dye in color layer

³ Whether screen layer contained UV screening agent

⁴ Peak Retention

⁵ CIELAB color difference determined by ISC.

35

These results illustrate that the invention is effective over a range of dye concentrations with polycarbonate color layers, but not with polymethyl methacrylate color layers.

40

45

50

55

Example 4

Example 4 illustrates different dyes and color layer polymeric matrix materials. The results are tabulated in Table IV.

Table IV

Sample	Matrix ¹	Dye ²	Screen ³	Time ⁴	Peak Reten ⁵	Delta E ⁶
4-1	PC	RED 5B	Yes	500	94	7(ISC)
4-A	PC	RED 5B	No	500	81	11(ISC)
4-B	PMMA	RED 5B	Yes	500	57	71(CSC)
4-C	PMMA	RED 5B	No	500	54	69(CSC)
4-2	PC	MACROLEX	Yes	1000	87	9(ISC)
4-D	PC	MACROLEX	No	1000	83	12(ISC)
4-E	PMMA	MACROLEX	Yes	500	58	57(CSC)
4-F	PMMA	MACROLEX	No	500	61	43(CSC)
4-3	PC	LUMOGEN	Yes	2000	82	9(ISC)
4-G	PC	LUMOGEN	No	2000	65	21(ISC)
4-H	PMMA	LUMOGEN	Yes	2000	85	15(CSC)
4-I	PMMA	LUMOGEN	No	2000	82	15(CSC)
4-J	PC	GREEN GOLD	Yes	500	65	23(ISC)
4-K	PC	GREEN GOLD	No	500	73	17(ISC)

¹ Matrix polymer

² Fluorescent dye

³ Whether screen layer contained UV screening agent

⁴ Exposure in hours

⁵ Peak Retention

⁶ CIELAB color difference determined by technique indicated in parentheses.

In Samples 4-1, 4-A, 4-2, 4-D, 4-3, and 4-G, when used in a color layer comprising polycarbonate the dyes exhibited substantially improved fluorescent durability with use of a screen layer as provided herein. However, in corresponding Samples 4-B, 4-C, 4-E, 4-F, 4-H, and 4-I the same dyes when used in a color layer comprising polymethyl methacrylate did not exhibit a substantial change in fluorescent durability with use of such a screen layer. In Samples 4-J and 4-K, GREEN GOLD dye was shown to not exhibit improved fluorescent durability in a color layer comprising polycarbonate used with a screen layer as provided herein.

Example 5

Example 5 illustrates the improved fluorescent durability attained in laminates of the invention in outdoor exposure. Each sample, about 7 X 18 centimeters in size, was adhered to an aluminum coupon which was mounted on a black painted panel facing upward at 45° from vertical and facing south and exposed for 10 months in Arizona.

In each sample, the screen layer consisted essentially of a 3 mil (75 micrometer) film of LUCITE 47K to which, in the indicated samples, 1.2 weight percent of TINUVIN 327 was added. The color layers consisted essentially of the indicated polymeric matrix material and 0.2 weight percent of the indicated fluorescent dye.

The results are tabulated in Table V.

Table V

Sample	Matrix ¹	Dye ²	Screen ³	Peak Reten ⁴	Delta E ⁵	Retain Fluor ⁶
5-1	PC	RED GG	Yes	64	21	76
5-A	PC	RED GG	No	53	30	65
5-B	PMMA	RED GG	Yes	62	22	83
5-C	PMMA	RED GG	No	69	22	85
5-2	PC	RED 5B	Yes	68	30	46
5-D	PC	RED 5B	No	45	35	32
5-3	PC	LUMOGEN	Yes	90	4	94
5-E	PC	LUMOGEN	No	73	16	83
5-4	PC	MACROLEX	Yes	76	21	88
5-F	PC	MACROLEX	No	70	23	80
5-5	PC	3G	Yes	92	5	89
5-G	PC	3G	No	63	26	71
5-H	PC	GREEN GOLD	Yes	48	51	18
5-I	PC	GREEN GOLD	No	47	42	47

¹ Matrix polymer

² Fluorescent dye

³ Whether screen layer contained UV screening agent

⁴ Peak Retention

⁵ CIELAB color difference determined by ISC

⁶ Retained Fluorescence

Claims

1. A fluorescent article characterized in that it comprises a color layer having first and second sides and a screen layer disposed to said first side of said color layer, wherein:

a) said color layer comprises daylight fluorescent dye dissolved in a polymeric matrix, said fluorescent dye comprising one or more of the following: thioxanthene dye, thioindigoid dye, benzoxazole coumarin dye, or perylene imide dye and said matrix being one or more of the following: polycarbonate, polyacrylic imide, polyester, or polystyrene; and

b) said screen layer being substantially transparent to visible light and comprising means for screening substantial portions of ultraviolet radiation incident thereto.

2. The article of claim 1 further characterized in at least one of the following:

a) said color layer contains between about 0.01 and about 1.0 weight percent of said dye; or

b) said color layer contains between about 0.05 and about 0.3 weight percent of said dye; or

c) said color layer is between about 50 and about 625 micrometers thick.

d) said color layer further comprises an additional coloring agent.

3. The article of claim 1 further characterized in at least one of the following:

a) said screen layer substantially blocks electromagnetic radiation having a wavelength below about 340 nanometers; or

b) said screen layer substantially blocks electromagnetic radiation having a wavelength below about 370 nanometers; or

c) said screen layer substantially blocks electromagnetic radiation having a wavelength below about 400 nanometers; or

d) said screen layer screens at least 50 percent of the ultraviolet radiation incident thereto.

4. The article of claim 1 further characterized in one of the following:

- 5 a) said screen layer is in direct contact with said color layer; or
b) said screen layer is bonded to said first side of said color layer with an intermediate layer of adhesive.

5. The article of claim 1 further characterized in that it further comprises a retroreflective base sheet disposed on said second side of said color layer.

10 6. The article of claim 5 further characterized in that said retroreflective base sheet comprises a monolayer of transparent microspheres and reflective means disposed on the side of said microspheres opposite said color layer.

15 7. The article of claim 1 further characterized in that said color layer has retroreflective elements formed on said second side.

8. The article of claim 7 further characterized in that said color layer is laminated directly to said screen layer and said retroreflective elements are cube-corner retroreflective elements.

20 9. The article of claim 1 further characterized in that said article is sufficiently flexible to be wound about a mandrel having a diameter of about 1 centimeter.

25 10. A fluorescent retroreflective article characterized in that it comprises a color layer having first and second sides and a screen layer disposed to said first side of said color layer, wherein:

- a) said color layer consists essentially of daylight fluorescent dye dissolved in a polymeric matrix, said fluorescent dye consisting essentially of one or more of the following: thioxanthene dye, thioindigoid dye, benzoxazole coumarin dye, or perylene imide dye and said matrix consisting essentially of one or more of the following: polycarbonate, polyacrylic imide, polyester, or polystyrene; and
30 b) said screen layer being substantially transparent to visible light and comprising means for screening substantial portions of ultraviolet radiation incident thereto;

said article comprising retroreflective elements on said second side of said color layer or a retroreflective base sheet disposed on said second side of said color layer.

35 **Patentansprüche**

1. Fluoreszierender Gegenstand, dadurch gekennzeichnet, daß dieser Gegenstand eine Farbschicht mit ersten und zweiten Seiten sowie eine Filterschicht umfaßt, die zu der ersten Seite der Farbschicht angeordnet ist, wobei:

- 40 a) die Farbschicht eine in einer Polymermatrix aufgelöste Tageslichtleuchtfarbe umfaßt, wobei der Fluoreszenzfarbstoff einen oder mehrere der folgenden Bestandteile umfaßt: Thioxanthenfarbstoff, Thioindigofarbstoff, Benzoxazol-Cumarinfarbstoff oder Perylen-Imidfarbstoff, und wobei es sich bei der Matrix um einen der folgenden Stoffe handelt: Polycarbonat, Polyacrylimid, Polyester oder Polystyrol; und wobei
45 b) die Filterschicht für sichtbares Licht im wesentlichen transparent ist, und wobei die Filterschicht ein Mittel zum Filtern eines wesentlichen Anteils der darauf auftreffenden Ultraviolettstrahlung umfaßt.

2. Gegenstand nach Anspruch 1, ferner gekennzeichnet durch mindestens eine der folgenden Bedingungen:

- 50 a) die Farbschicht umfaßt zwischen etwa 0,01 und etwa 1,0 Gewichtsprozent des Farbstoffs; oder
b) die Farbschicht umfaßt zwischen etwa 0,05 und etwa 0,3 Gewichtsprozent des Farbstoffs; oder
c) die Farbschicht weist eine Dicke zwischen etwa 50 und etwa 625 Mikrometern auf;
d) die Farbschicht umfaßt ferner ein zusätzliches Farbmittel.

55 3. Gegenstand nach Anspruch 1, ferner gekennzeichnet durch mindestens eine der folgenden Bedingungen:

- a) die Filterschicht blockiert im wesentlichen elektromagnetische Strahlungen mit einer Wellenlänge unter etwa 340 Nanometern; oder

b) die Filterschicht blockiert im wesentlichen elektromagnetische Strahlungen mit einer Wellenlänge unter 370 Nanometern; oder

c) die Filterschicht blockiert im wesentlichen elektromagnetische Strahlungen mit einer Wellenlänge unter etwa 400 Nanometern; oder

d) die Filterschicht filtert mindestens 50 Prozent der darauf auftreffenden Ultraviolettstrahlung.

4. Gegenstand nach Anspruch 1, ferner gekennzeichnet durch eine der folgenden Bedingungen:

a) die Filterschicht befindet sich in direktem Kontakt mit der Farbschicht; oder

b) die Filterschicht ist mit einer Klebstoff-Zwischenschicht mit der ersten Seite der Farbschicht verbunden.

5. Gegenstand nach Anspruch 1, ferner dadurch gekennzeichnet, daß der Gegenstand eine retroreflektierende Grundschicht umfaßt, die auf der zweiten Seite der Farbschicht angeordnet ist.

6. Gegenstand nach Anspruch 5, ferner dadurch gekennzeichnet, daß die retroreflektierende Grundschicht eine Monoschicht transparenter Mikrosphären und Reflexionsmittel aufweist, das sich auf der der Farbschicht entgegengesetzten Seite der Mikrosphären befindet.

7. Gegenstand nach Anspruch 1, ferner dadurch gekennzeichnet, daß die Farbschicht retroreflektierende Elemente aufweist, die auf der zweiten Seite ausgebildet sind.

8. Gegenstand nach Anspruch 7, ferner dadurch gekennzeichnet, daß die Farbschicht direkt auf die Filterschicht geklebt ist, und wobei es sich bei den retroreflektierenden Elementen um retroreflektierende Würfel-Ecken-Elemente handelt.

9. Gegenstand nach Anspruch 1, ferner dadurch gekennzeichnet, daß der Gegenstand eine ausreichende Flexibilität aufweist, so daß er um einen Dorn mit einem Durchmesser von etwa 1 Zentimeter gewickelt werden kann.

10. Fluoreszierender, retroreflektierender Gegenstand, dadurch gekennzeichnet, daß dieser Gegenstand eine Farbschicht mit ersten und zweiten Seiten sowie eine Filterschicht umfaßt, die zu der ersten Seite der Farbschicht angeordnet ist, wobei:

a) die Farbschicht eine in einer Polymermatrix aufgelöste Tageslichtleuchtfarbe umfaßt, wobei der Fluoreszenzfarbstoff einen oder mehrere der folgenden Bestandteile umfaßt: Thioxanthinfarbstoff, Thioindigoanilinfarbstoff, Benzoxazol-Cumarinfarbstoff oder Perylen-Imidfarbstoff, und wobei es sich bei der Matrix um einen der folgenden Stoffe handelt: Polycarbonat, Polyacrylimid, Polyester oder Polystyrol; und wobei

b) die Filterschicht für sichtbares Licht im wesentlichen transparent ist, und wobei die Filterschicht ein Mittel zum Filtern eines wesentlichen Anteils der darauf auftreffenden Ultraviolettstrahlung umfaßt;

wobei der genannte Gegenstand auf der zweiten Seite der Farbschicht retroreflektierende Elemente aufweist oder eine retroreflektierende Grundschicht, die auf der zweiten Seite der Farbschicht angeordnet ist.

Revendications

1. Objet fluorescent, caractérisé en ce qu'il comprend une couche de couleur ayant un premier et un deuxième côté et une couche-écran disposée sur ledit premier côté de ladite couche de couleur, dans lequel:

a) ladite couche de couleur comprend un colorant fluorescent à la lumière du jour, dissous dans une matrice polymère, ledit colorant fluorescent comprenant un ou plusieurs des colorants suivants : colorant thioxanthène, colorant thioindigoïde, colorant benzoxazole-coumarine ou colorant pérylène-imide et ladite matrice étant constitué d'un ou plusieurs des polymères suivants : polycarbonate, imide polyacrylique, polyester ou polystyrène; et

b) ladite couche-écran étant essentiellement transparente à la lumière visible et comprenant un moyen pour arrêter des fractions importantes du rayonnement ultraviolet qui l'atteint.

2. Objet selon la revendication 1, caractérisé en outre par l'une des caractéristiques suivantes :

a) ladite couche de couleur contient entre environ 0,01 et environ 1,0% en poids dudit colorant; ou

b) ladite couche de couleur contient entre environ 0,05 et environ 0,3% en poids dudit colorant; ou

c) ladite couche de couleur a une épaisseur comprise entre environ 50 et environ 635 micromètres;

d) ladite couche de couleur comprend, en outre, un agent colorant supplémentaire.

3. Objet selon la revendication 1, caractérisé en outre par au moins l'une des caractéristiques suivantes :

- 5 a) ladite couche-écran arrête essentiellement les rayonnements électromagnétiques ayant une longueur d'onde inférieure à environ 340 nanomètres; ou
b) ladite couche-écran arrête essentiellement les rayonnements magnétiques ayant une longueur d'onde inférieure à environ 370 nanomètres; ou
10 c) ladite couche-écran arrête essentiellement les rayonnements électromagnétiques ayant une longueur d'onde inférieure à environ 400 nanomètres; ou
d) ladite couche-écran arrête au moins 50% des rayonnement ultraviolets qui l'atteignent.

4. Objet selon la revendication 1, caractérisé en outre par l'une des caractéristiques suivantes :

- 15 a) ladite couche-écran est en contact direct avec ladite couche de couleur; ou
b) ladite couche-écran est fixée audit premier côté de ladite couche de couleur par une couche adhésive intermédiaire.

5. Objet selon la revendication 1, caractérisé en outre en ce qu'il comprend en outre une feuille de base réfléchissante, disposée sur ledit deuxième côté de ladite couche de couleur.

6. Objet selon la revendication 5, caractérisé en outre en ce que ladite feuille de base réfléchissante comprend une monocouche de microsphères transparentes et un moyen réfléchissant disposé sur le côté desdites microsphères opposés à ladite couche de couleur.

7. Objet selon la revendication 1, caractérisé en outre en ce que ladite couche de couleur a des éléments réfléchissants disposés sur ledit deuxième côté.

8. Objet selon la revendication 7, caractérisé en outre en ce que ladite couche de couleur est directement stratifiée sur ladite couche-écran et que lesdits éléments réfléchissants sont des éléments réfléchissants à angles de cube.

9. Objet selon la revendication 1, caractérisé en outre en ce que ledit objet est suffisamment flexible pour être enroulé sur un mandrin ayant un diamètre d'environ 1 cm.

10. Objet réfléchissant fluorescent, caractérisé en ce qu'il comprend une couche de couleur ayant un premier et un deuxième côtés et une couche-écran disposée sur ledit premier côté de ladite couche de couleur, dans lequel :

- a) ladite couche de couleur est constituée essentiellement d'un colorant fluorescent à la lumière du jour, dissous dans une matrice polymère, ledit colorant fluorescent comprenant essentiellement un ou plusieurs des colorants suivants : colorant thioxanthène, colorant thioindigoïde, colorant benzoxazole-coumarine ou colorant pérylène-imide et ladite matrice étant constituée essentiellement d'un ou plusieurs des polymères suivants : polycarbonate, imide polyacrylique, polyester ou polystyrène; et
40 b) ladite couche-écran étant essentiellement transparente à la lumière visible et comprenant un moyen pour arrêter des fractions importantes du rayonnement ultraviolet qui l'atteint; ledit objet comprenant des éléments réfléchissants sur ledit deuxième côté de ladite couche de couleur ou une feuille de base réfléchissante disposée sur ledit deuxième côté de ladite couche de couleur.

50

55

